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HIGH TEMPERATURE EVALUATION OF NEW FERROELASTIC TOUGHENED CERAMIC MATERIALS

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FINAL REPORT

DEPARTMENT OF ARMY
CONTRACT NO. #DAAL04-87-C-0058

FOR
SBIR PHASE I

AUGUST 15, 1987 - FEBRUARY 15, 1988

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ABSTRACT

The toughness behavior of ceria tetragonal zirconia polycrystalline (TZP) ceramics was investigated relative to the effect of various dopants (coded as dopants A, B and C in this report due to pending patent applications). Additions of dopant A enhanced the toughness of zirconia ceramics, dopant B suppressed the fracture toughness and, dopant C had little effect on toughness. High temperature strength retention in zirconia ceramics containing dopant A suggest that mechanisms other than transformation toughening are operative. Switching of x-ray peak intensities showed that the tetragonal zirconia used in the present study is ferroelastic. Phase I results showed that the present processing approach does not result in ferroelastic toughening as the principal toughening mechanism operative. Potential reasons for this have been identified and appropriate processing changes will be made in Phase II. Additional research is needed to show whether crack deflection is operative in the doped ceramics due to the formation for a second phase.

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INTRODUCTION

Background

Prior work at Ceramatec showed that tetragonal zirconia is a ferroelastic material[1,2]. Phenomenologically, ferroelastic materials are analogous to ferroelectric materials. Ferroelectric materials are characterized by the existence of nonzero polarization, P, in the absence of applied field, E, and existence of a P-E hysteresis. Energy enclosed by the hysteresis loop is the electrical energy dissipated (converted to heat). Ferroelastic materials are those in which the respective parameters are stress, σ, (instead of E) and strain, ε, (instead of P). By analogy ferroelastic materials have the potential to convert mechanical energy into heat, hence the potential toughening mechanism, i.e., mechanical energy can be dissipated in other ways instead of contributing towards crack extension. Both these types of materials are termed ferroic materials. (Actually, ferromagnetic materials are also ferroic materials, but are omitted in the present discussion.)

Ferroic properties of materials are known to depend upon the type and the amount of minor constituents in a complex manner. Dielectric permittivity of many commercial $BaTiO_3$-based and PZT-based ceramics can be drastically altered by the addition of extremely small amounts of dopants. In fact the majority of the manufacturers of capacitors, PZT transducers, etc., incorporate numerous proprietary additives to the base materials in order to engineer properties. For example, there are very minor compositional differences between hard and soft PZT.

Since tetragonal zirconia is ferroelastic as shown recently[1,2], its properties such as the coercive stress (stress necessary to change the orientation of domains) are expected to depend upon the chemistry of the material in a complicated, and at present, unknown manner. Since the

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toughness of the material (that contribution which results from the ferroic nature of the material) is expected to depend upon the coercive stress, chemistry of the material is expected to be important in determining the mechanical properties. The various dopants that have been added to zirconia in a prior program funded by Ceramatec were with the express purpose of altering the mechanical properties, in particular to enhance the ferroic contribution to the toughness. Enhancement of the ferroic contribution should in principle lead to materials capable of exhibiting improved properties at elevated temperatures since the cubic --> tetragonal transformation temperature (Curie temperature) is typically greater than 1600°C.

The choice of dopants, whose concentration was typically below 2%, with concentrations as low as 0.1%, were chosen on the basis of ionic radii and valence. Such rationale is often used in doping ferroelectric materials in which strain at the atomic level and local electrostatic fields are known to influence properties. Several additives were identified at Ceramatec in the in-house work which led to increased toughness in zirconia, a based ceramic. One particular dopant increased the toughness of ceria-stabilized tetragonal zirconia to approximately 20 $MPa.m^{1/2}$ at room temperature. This particular dopant, however, enhanced the transformability of the tetragonal phase to the monoclinic polymorph thereby increasing the transformation toughening contribution. Another dopant (coded "dopant A" in this report due to pending patent applications) was found to be effective in enhancing the toughness without significantly increasing the transformability of tetragonal zirconia. It was, for example, observed that toughness values as high 16 $MPa.m^{1/2}$ could be achieved by adding approximately 2 wt% of dopant A to CeTZP. This material after surface grinding did not show formation of any monoclinic zirconia but did exhibit x-ray intensity reversal of (200)/(002) doublet, which occurred due to ferroelastic domain switching. These results suggested that in A-doped CeTZP, the

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ferroelastic contribution is probably significant and is the logical candidate material for elevated temperature applications. It is for this reason that A-doped ZrO_2 was chosen for Phase I SBIR work funded by the Army. As mentioned previously, ferroic properties of materials depend upon the chemistry in a complicated and often unknown manner. As a consequence, properties do depend on processing parameters and until the principal factors are identified, a large variability in properties is to be expected. An exploratory project was proposed in Phase I with high temperature performance as the primary goal.

Objectives of Phase I

Specific technical objectives of Phase I were: (1) to fabricate selected compositions and evaluate the strength retention from 750°C to 1100°C, (2) use the resulting information to guide a fabrication and evaluation iteration, (3) select one or more compositions for stressing rate and static fatigue tests in the 850-1100°C temperature range, (4) collaborate with the Army Materials Technology Laboratory to conduct the testing, and (5) analyze the results and assess the technology potential.

As mentioned in the foregoing, mechanical properties of ferroelastic materials are expected to be sensitive to composition and processing. Transformation toughening is also known to depend upon composition and microstructure. However, the contribution of transformation from tetragonal-->monoclinic is expected to decrease with increasing temperature and totally vanish in the stability range of the tetragonal phase which can be as low as 700°C to 800°C in doped materials. Numerous experimental researches are in accord with this expectation. By contrast, the contribution of ferroelasticity to toughening is expected to increase with increasing temperature (since coercive stress decreases with increasing temperature) up to temperatures

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in the vicinity of the Curie temperature above which the toughening effect will be nonexistent. In most doped zirconias, the Curie temperature is well in excess of 1600°C. Hence, toughening contribution due to ferroelasticity is expected to be present at fairly high temperatures. This suggests that the transformation toughening concept has no hope of yielding materials with high K_c at elevated temperatures. However, ferroelasticity, in principle, may provide the requisite properties at elevated temperatures. Data of Ingel et.al.[3], on single crystals of tetragonal zirconia (which are actually polydomain materials) shows that excellent properties can be retained to approximately 1600°C. Later studies have shown that these materials do not transform to the monoclinic phase[4].

Zirconia ceramics, as they are fabricated in most studies including the present SBIR program, suffer from the fact they show substantial amount of transformation toughening. In the present work, the materials used were of this type. However, for the work proposed in Phase II, other approaches for fabricating zirconia and other related materials from the standpoint of enhancement of high temperature properties will be explored. These are discussed in the Phase II proposal.

The present work was initiated with an objective to develop a material which exhibits strength in excess of 500 MPa and toughness in excess of 7 MPa.m$^{1/2}$ above 750°C. The specific tasks proposed in the work plan are listed in Table 1.

Table 1
Work Plan for Phase I

Task	Month						
	0	1	2	3	4	5	6
1. Fabrication of modified Ce-TZP ceramics	=====>						
2. Preliminary room temperature and elevated temperature (up to 1100°C) strength and toughness testing			=====>				
3. Fabrication of modified Ce-TZP based upon results of Task 2			=======>				
4. Strength, toughness & static fatigue testing to 1100°C				=====>			
5. Fractography, characterization and data analysis		=================>					
6. Final report						===>	

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EXPERIMENTAL PROCEDURES

Powder and Parts Fabrication

Previous in-house work at Ceramatec, Inc. has identified A as a dopant which when incorporated in minor amounts, enhances the room temperature toughness to as high as 16 $MPa.m^{1/2}$ without strength degradation. On ground surfaces, no monoclinic phase was observed. However, the intensity of (002) peak increased while that of (200) peak decreased, characteristic of ferroelastic switching. For this reason, it was assumed that this material should exhibit a significant proportion of ferroelastic contribution to toughening. Two other dopants selected for the study are coded B and C in this report. The objective was to determine if the ionic radius of the dopant influences the toughening behavior of the doped ZrO_2. The dopants were introduced at three levels: 1 wt%, 2 wt%, and 3 wt%. These are designated as A-1, A-2, A-3; B-1, B-2, B-3; and C-1, C-2, C-3 for dopants A, B, and C, respectively. The undoped powder was designated by U. Compositions used in Phase I are given in Table 2.

Table 2
Dopants Added to Ceria TZP Ceramics

Concentration (wt.%)	Dopant-A	Dopant-B	Dopant-C
0	U	U	U
1	A-1	B-1	C-1
2	A-2	B-2	C-2
3	A-3	B-3	C-3

The dopants were added to spray-dried Ce-TZP powder of composition: 12 mol% CeO_2-88 mol% ZrO_2 to which 10 wt% Al_2O_3 was added. This powder is made for commercial products[1]. Dopants were introduced by reslurrying the powder along with dopants in a small vibratory mill. This procedure was chosen for convenience even though a better approach would involve the incorporation of the dopants prior to spray drying. In future work, the dopants will be introduced prior to spray drying. In the present experiments, powder mixtures (in water) were vibratory milled using zirconia milling media. Subsequently, the powder was pan dried, screened through an 80 mesh sieve and uniaxially pressed at 35 MPa into bar shaped samples followed by isostatic pressing at 135 MPa.

Sintering

All of the samples were sintered in air in an electric furnace equipped with molybdenum disilicide elements. Samples were placed on alumina setters which were covered with CeTZP powder as setter sand to prevent any possible reaction between the samples and the setters. Also, some CeTZP powder was sprinkled on every sample (upon which other samples were stacked) to prevent samples from sticking to each other. Samples were sintered at 1500°C for 2 hours. Some problems were encountered during the early stages of the program with regard to cracking. However, these were corrected allowing dense, crack-free samples to be fabricated for all compositions. However, sufficient powder was not available with dopant C at 1% level for doing testing at room as well as elevated temperatures.

Sample Preparation

Strength bars were prepared by diamond grinding sintered samples. All four faces were ground. The cross-sectional area of each sample after grinding was 3mm X 4mm. Two long edges of

[1]*CZ203, Ceramatec, Inc. (Salt Lake City, UT).

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the samples (one 4mm wide face) were chamfered to minimize failures during testing from edges. The chamfered side was made the tensile side during room temperature and elevated temperature flexural strength testing.

Fracture toughness was measured using single edge notched beam (SENB) specimens in bending. Even though techniques such as double cantilever beam (DCB) and short rod are preferable since a sharp crack can be introduced in these samples, SENB geometry was chosen for ease of testing at high temperatures. Prior work at Ceramatec on ceria-doped zirconia has shown that at room temperature the SENB technique in fact gives lower K_c than the DCB method. Thus, in this system, SENB is expected to give a conservative estimate of K_c. For this reason, the use of SENB should be acceptable.

SENB samples were fabricated by machining a thin notch (notch width = 0.216mm) which extended halfway through the sample. (Some samples, however, were notched with a thicker blade which resulted in notch width of 0.47mm).

Room temperature fracture toughness was also measured using the DCB technique. DCB samples were fabricated by grinding thin beam shaped samples on all four sides (excepting the ends which were diamond cut to ensure orthogonality). Holes were drilled for loading and the samples were slotted to prevent the deviation of the crack from the plane of symmetry.

Characterization
Density and Phase Content
Density of selected samples from each batch of sintered samples was measured by water immersion. All parts were tested in the as-sintered unground condition.

Samples were examined by x-ray diffraction using Cu K radiation in the as-fired and surface ground condition. The objective was to determine the amount of the monoclinic phase in the as-fired and ground condition as well as to determine the extent of ferroelastic domain switching.

Mechanical Testing

Flexural Strength: Flexural strength was measured in four point bending with outer and inner spans equal to 40mm and 20mm, respectively. Cross-sectional dimensions were 3mm X 4mm as mentioned earlier. Elevated temperature strength testing was conducted under the direction of Mr. Jeffrey Swab of the U.S. Army Materials Technology Laboratory. Strength was measured at 25°C, 750°C, 900°C, 1000°C and 1100°C. Samples were fractured under a cross head speed of 0.5mm/min. Typically four samples were tested for strength under a given set of conditions.

Fracture Toughness: Fracture toughness values were obtained using the double cantilever beam technique at room temperature. The pertinent equation which related the toughness, K_C, to the critical load, P_C, the crack length, l, and specimen dimensions is given by[5]

$$K_C = P_C l \sqrt{\frac{12}{wbh^3} (1+1.32(h/l)+0.54(h/l)^2)} \qquad (1)$$

where P_C = load at the condition of criticality
    l   = crack length measured from the loading holes
    w   = thickness of the sample
    b   = web thickness
and   h   = half height of the sample (actually, the second longest dimension of the sample in the geometry used).

Figure 1 shows a schematic of a typical sample. The procedure used for K_C measurement using DCB technique was as follows:

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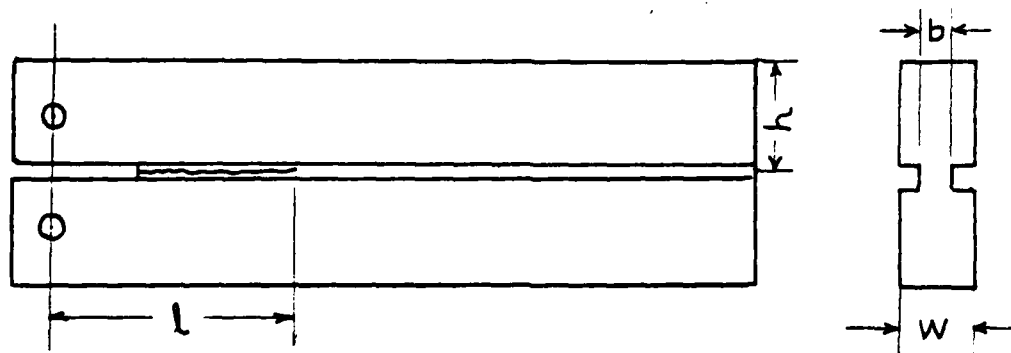
Figure 1: A schematic showing the double cantilever beam (DCB) sample used for the measurement of fracture toughness, K_{Ic}.

1) A notch with a chevron tip for easy crack initiation was machined in each sample.

2) Subsequently, each sample was pulled in tension using appropriate loading fixture until a small abrupt drop in load occurred indicative of the formation of a crack at the root of the notch.

3) Sample was unloaded, sprayed with fluorescent dye for determining the crack length, say l_1.

4) The sample was again inserted in the test fixture and pulled in tension until load dropped indicating crack growth. The load at instability was recorded, say P_{c1}.

5) Using P_{c1} and l_1 and specimen dimensions, K_c was calculated via Equation (1).

6) The sample was unloaded for the measurement of the crack length and the procedure was repeated. In this manner as many as 15 data points could be obtained on a single sample, particularly in materials exhibiting high K_c.

K_C was also measured using SENB specimens at room temperature (for comparison with DCB) and at elevated temperatures. Toughness was calculated using Equation (2)[6].

$$K_C = (P_C S/Bw^{3/2})\left(\frac{3(a/w)^{1/2}[1.99-(a/w)(1-(a/w))(2.15-3.93(a/w)+2.7(a/w)^2)]}{2(1+2(a/w))(1-(a/w))^{3/2}}\right) \quad (2)$$

where a = depth of the notch
      w = width of the sample
      B = thickness of the sample
      S = span
and P_C = fracture load

Stepped-Temperature Stress-Rupture Tests: Typically four samples of each composition were subjected to a stepped-temperature stress-rupture test. This test was performed at AMTL under the direction of Mr. Jeffrey Swab. The test consisted of loading a test bar to a predetermined stress while increasing the ambient temperature through a series of steps. In this case the temperature history was a 24 hour hold at 750°C, 900°C, 1000°C and 1100°C with a 10 minute ramp between steps. The point (i.e., temperature and time at temperature) at which a sample failed was noted and the next sample was subjected to a lower stress.

Fractographic Observations

Fracture surfaces were examined both under an optical microscope and a scanning electron microscope. The objectives were: (1) to estimate the grain size of the material, (2) to identify the fracture origin, (3) to determine if the mode of fracture is transgranular or intergranular, and (4) to estimate potential crack interaction with microstructural features.

RESULTS AND DISCUSSION

Density

Table 3 gives bulk density of sintered parts of various compositions. Most of the samples were sintered to the stage of closed porosity except A-3. The baseline material had the highest density (5.83 g/cm^3) while the samples containing dopants A, B, & C had lower density, the effect being more pronounced with dopant A. The addition of these dopants to zirconia is expected to suppress the densification of zirconia. Recent work at Ceramatec, however, has shown that densities in excess of 99% of theoretical can be obtained for CeTZP doped with up to 4 wt. % A. Future work will address the densification kinetics of doped (with dopants A, B, C and some other dopants) zirconia since for the achievement of improved properties it is essential to achieve high density.

Table 3
Bulk Density of Sintered Compositions

Composition	Density (g/cm^3)	Theoretical (%)
Baseline Material (U)	5.83 ± 0.01	98.8%
A1	5.76 ± 0.00	97.6%
A2	5.57 ± 0.00	94.4%
A3	5.36 ± 0.03	90.8%
B1	5.77 ± 0.01	97.8%
B2	5.76 ± 0.01	97.6%
B3	5.71 ± 0.01	96.8%
C1	5.78 ± 0.01	97.9%
C2	5.77 ± 0.01	97.8%
C3	5.72 ± 0.01	96.9%

Fracture Toughness

Fracture toughness was measured by DCB and SENB techniques at room temperature. DCB testing was performed on 2 samples from every batch. On each sample, several data points (as many as 15) were obtained. Only one sample from each batch was used for SENB testing. Table 4 gives the toughness of the samples measured by these two techniques at room temperature. SENB data obtained on samples with wide notches are given in parentheses. As shown in the table, the samples with wider notches yield apparently higher values of Kc, as expected.

Dopant A enhanced the toughness over the baseline material. Prior work has shown that fracture toughness (DCB) as high as 16 $MPa.m^{1/2}$ (DCB) can be obtained in samples in which the dopant is well distributed. Table 4 shows that dopant B drastically lowers the K_C while dopant C moderately suppresses it.

Table 4.
Room Temperature Fracture Toughness

Material	K_C ($MPa.m^{1/2}$)	
	DCB Technique	SENB* Technique
Baseline, U	10.4 ± 0.3	(15.1)
A1	11.9 ± 0.1	(16.7)
A2	14.1 ± 1.5	--
A3	12.3 ± 0.2	(10.4)/14.5**
B1	5.9 ± 0.1	(12.4)
B2	5.6 ± 0.3	(12.9)
B3	5.8 ± 0.3	(12.4)
C1	9.1 ± 0.3	12.9
C2	9.4 ± 0.2	11.4
C3	9.0 ± 0.1	9.9

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* SENB values in parentheses based on samples with wider notches.
** This sample yielded high value despite narrow notch
    suggesting that the toughness was indeed high.

These data suggest that the effect of the various dopants on K_C^- is indeed quite profound. As mentioned earlier, ferroic properties of materials are known to be sensitive to impurities, intentionally added or otherwise. Since these zirconia materials also exhibit a substantial transformation toughening effect, it must be concluded that the dopants also influence the transformability of zirconia grains. The significance of this is indeed profound since it means it should be possible to engineer the properties of TZP ceramics through careful addition of minor impurities, whether the toughening effect comes from transformation of tetragonal to monoclinic, ferroelastic domain switching or both mechanisms. The Phase II proposal will address specifics of how the ferroelastic contribution can be enhanced.

Fracture toughness was measured over a range of temperatures between 750°C and 1100°C using the SENB technique. At 1100°C, toughness values as high as 5.0 $MPa.m^{1/2}$ were measured. These data are given in Table 5.

General observations that can be made from the data given in Table 5 are: (1) Above 750°C, the K_C values are not strongly dependent upon temperatures; (2) The K_C values are typically (approximately) 5.0 $MPa.m^{1/2}$. This is an important point since the contribution of transformation toughening to the overall toughness is negligible above 750°C. At the same time, prior work has shown that cubic zirconia has a toughness on the order of (approximately) 2 to 2.5 $MPa.m^{1/2}$. Clearly, the present materials, which are essentially 100% tetragonal zirconia and do not form any monoclinic phase when tested above approximately 750°C, owe their higher toughness to mechanisms other than transformation toughening. Since the Curie temperature is well over 1600°C, •the implication is that some of the toughening must have resulted from ferroelastic domain switching. In Phase II,

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Table 5.

Elevated Temperature Fracture Toughness (MPa·m$^{1/2}$)

Material	750°C	900°C	1000°C	1100°C
Baseline (U)	(A.3)*	(6.0)	(5.3)	(5.1)
A-1	(3.6)	(4.8)	(6.8)	(4.5)
A-2	(4.5)	(5.1)	(5.2)	(3.9)
A-3	--	--	(4.0)	(4.4)
B-1	(8.5)	(4.8)	(4.3)	(4.3)
B-2	(4.8)	(5.8)	--	(4.3)
B-3	(2.8)	(4.5)	(4.3)	(4.0)
C-1	3.9	5.0	--	3.7
C-2	5.2	6.4	5.7	5.0
C-3	--	--	--	--

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* Numbers in parentheses are those with wide notches.

the objective will be to identify parameters which, when optimized, enhance this contribution. (3) Composition C-2 has toughness values as high as 6.4 MPa.m$^{1/2}$ at 900°C. This is the highest K_C measured at 900°C and with a narrow notch. The same composition had a K_C of 9.4 MPa.m$^{1/2}$ at room temperature. Clearly, the ferroelastic contribution must be high in this material. Table 6 gives a comparison between K_C measured at room temperature and average value (between 750°C and 1100°C) at elevated temperatures.

Strength

The samples from the first iteration were tested for strength (at the U.S. Army Materials Technology Laboratory under the direction of Mr. Jeffrey Swab) at 750°C, 900°C, 1000°C, and 1100°C. These data are given in Table 7 along with the room temperature strength data.

Table 6.

Comparison K_C at Room Temperature and Elevated Temperature

Material	K_C (DCB) at Room Temp. (MPa.m$^{1/2}$)	*K_C (SENB) at Elevated Temp. (MPa.m$^{1/2}$)
Baseline-U	10.4	5.2
A-1	11.9	4.9
A-2	14.1	4.7
A-3	12.3	4.2
B-1	5.9	5.5
B-2	5.6	5.0
B-3	5.8	3.9
C-1	9.1	4.2
C-2	9.4	5.6
C-3	9.8	--

----

* Average K_C between 750°C and 1100°C.

Table 7.

Fracture Strength Measurements

Material	25°C	750°C	900°C	1000°C	1100°C
Baseline	635+20	250+30	220+30	230+2	220+5
A-1	650+60	250+20	230+50	260+10	235+20
A-2	530+45	240+5	210+30	200+10	195+7
A-3	340+45	220+40	200+10	200+20	220+10
B-1	560+40	220+10	200+10	200+10	170+10
B-2	660+40	240+10	230+20	220+30	190+15
B-3	540+60	195+10	190+25	180+10	140+20
C-1	600+20	--	--	--	--
C-2	610+20	230+70	250+10	240+30	230+15
C-3	550+15	250+10	240+10	230+7	220+20

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As shown in Table 7, the strength decreased with increasing temperature. Above 750°C, however, strength was essentially independent of temperature. Thus, despite lower strengths, it is clear that the strength is essentially invariant with temperature. Clearly, one must enhance these plateaus of strength to higher values. This, in principle, can be achieved by carefully controlling the dopant levels and thermal treatment procedures. The second iteration was later undertaken to address these issues.

In Table 8, the room temperature strength is compared with (average) elevated temperature strength. It is seen that 33 to 62% of the room temperature strength is retained at high temperatures.

Additional Compositions

A second series was initiated after the completion of testing of the first series. For the second series, samples were made with dopants A and C only. No samples with dopant B were

Table 8.
High Temperature Retained Strength

Material	Room Temp. Strength (MPa)	Average* High Temp. Strength (MPa)	% Retained Strength
Baseline-U	635	230	36%
A-1	650	240	37%
A-2	530	210	40%
A-3	340	210	62%
B-1	560	200	35%
B-2	660	220	33%
B-3	540	180	33%
C-1	600	--	--
C-2	610	240	39%
C-3	550	230	42%

----

* Average strength between 750°C and 1100°C.

made since this dopant decreased the K_c at room temperature. Samples containing 0.5% and 1.5% of the dopants were made. Also made were samples doped with A at 1.0% level. This is essentially a duplicate of composition used in the first series. Table 9 gives compositions and nomenclature. The densities on the samples from the second series are shown in Table 10.

Room temperature fracture toughness testing was performed using DCB and SENB technique. These data are given in Table 11. No high temperature testing was done.

Strength in flexure was measured at 25°C, 750°C, 900°C, 1000°C and 1100°C. In all compositions, except one, the strength decreased substantially with increasing temperature. That exception was A'-1 which had a strength of 550 MPa at room temperature and had a strength of 400 MPa at 1100°C. This composition is the same as the A-1 of the first series. Clearly, whatever minor difference in the sintering schedule and dopant distribution, at present unknown, that occurred led to such a drastic difference is strength characteristics of apparently similarly prepared material. A'-1 also has slightly higher density compared to A-1 which may be partially responsible for higher strength. Dopant A does not completely go into solution

Table 9.
Additional Ce-TZP Compositions (Second Series)

Dopant A		Dopant C	
Nomenclature	Composition (Dopant level-wt%)	Nomenclature	Composition (Dopant level-wt%)
A'-1	1%	—	—
A-0.5	1/2%	C-0.5	1/2%
A-1.5	1-1/2%	C-1.5	1-1/2%

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Table 10.
Bulk Densities for Second Series

Material	Density (g/cm^3)
A'-1	5.83 + 0.01
A-0.5	5.80 $\mp$ 0.00
A-1.5	5.51 $\mp$ 0.01
C-0.5	5.80 + 0.02
C-1.5	5.78 $\mp$ 0.00

with CeTZP. Plate-like precipitates can be clearly seen in SEM micrographs. Recent work has identified that the precipitates are an aluminate due to a reaction with the dopants. These precipitates may provide toughening due to crack deflection in addition to transformation and ferroelastic mechanisms. The contribution of crack deflection to the overall toughness is not expected to diminish with increasing temperature which is a problem with transformation toughening. Phase II research will concentrate on promoting ferroelastic switching and crack deflection, mechanisms which will be operative at temperatures in excess of 1000°C.

It is clear from the toughness data of the second series that mechanical properties are sensitive to both dopant levels and processing. However, when one compares this sensitivity of properties to processing with that routinely observed in ferro-

Table 11.

Second Series Fracture Toughness at Room Temperature

Material	K_C (DCB) ($MPa.m^{1/2}$)	K_C (SENB) ($MPa.m^{1/2}$)
A'-1	14.5 + 0.6	15.2 + 0.3
A-0.5	13.6 $\mp$ 0.6	14.5 $\mp$ 0.4
A-1.5	11.5 $\mp$ 0.4	12.7 $\mp$ 0.4
C-0.5	10.7 + 0.2	16.7 + 0.1
C-1.5	9.7 $\mp$ 0.2	13.5 $\mp$ 0.0

electric and piezoelectric ceramics, it is understood that this is typical of ferroic materials. The fact that moderately high strength values can be realized at elevated temperatures is apparent from these results (see Table 12). The major task, to be addressed in Phase II, is to identify parameters which consistently yield improved properties at elevated temperatures. Strength data from second series are given in Table 12. For the A'-1 composition, 73% of the room temperature strength was retained at 1100°C.
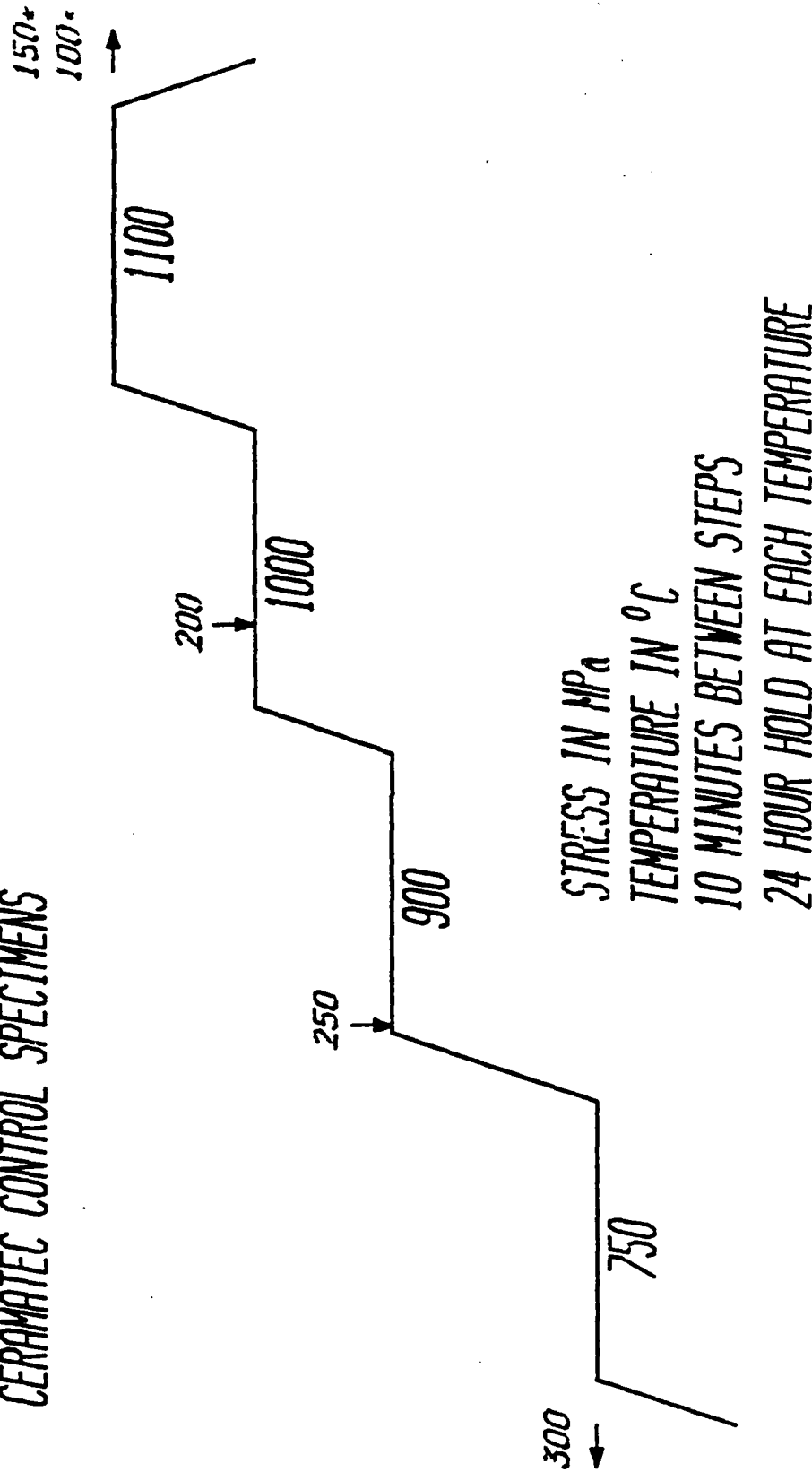
Stepped-Temperature Stress-Rupture Tests (STSR)

Stepped-temperature stress-rupture testing was performed on a few samples with dopants A and C. These data are shown in Figures 2 to 9. Within the experimental error, all samples behaved essentially in the same manner. Sample A-2 showed the best performance. Additional experiments would be necessary to determine if there are any differences. In Phase II, experiments will also be done on fully stabilized (cubic) zirconia. The objective will be to determine if any toughening results from the ferroelasticity since the cubic phase cannot exhibit ferroelasticity.

Table 12.
Second Series Strength

Material	25°C	750°C	900°C	1000°C	1100°C
A'-1	550+40	470+9	370+10	370+20	400+10
A-0.5	560+10	430+10	200+5	200+4	190+10
A-1.5	520+20	230+10	170+15	100+4	95+10
C-0.5	620+10	230+60	240+10	250+10	220+7
C-1.5	590+6	440+90	—	—	230+20

Figure#2: Stress rupture test of sample-U.

STEPPED TEMPERATURE STRESS RUPTURE

CERAMATEC υ SPECIMENS

STRESS IN MPa
TEMPERATURE IN °C
10 MINUTES BETWEEN STEPS
24 HOUR HOLD AT EACH TEMPERATURE

150

1100

200

225

1000

900

750

250
250
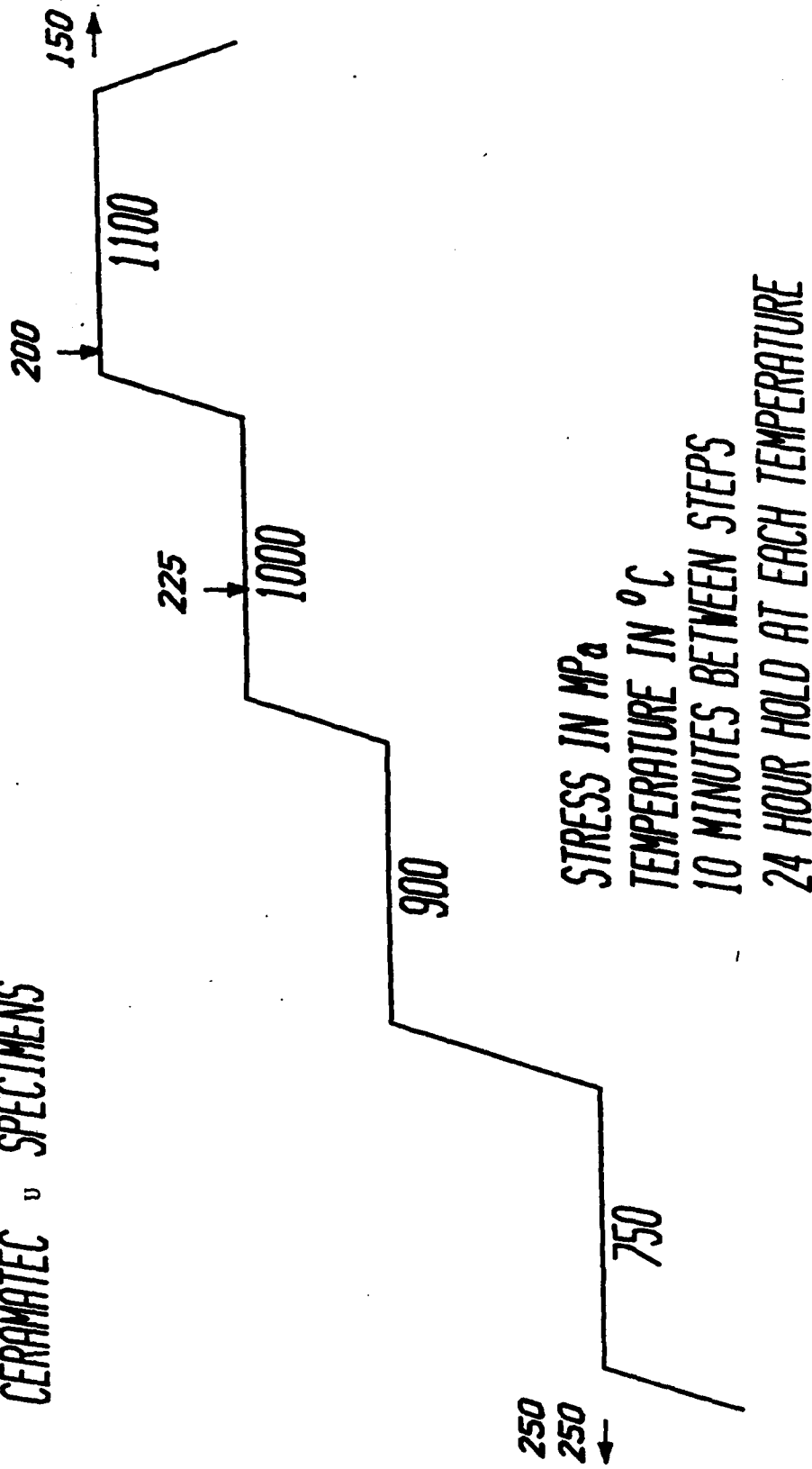
Figure#3: Stress rupture test of sample-U.

STEPPED TEMPERATURE STRESS RUPTURE
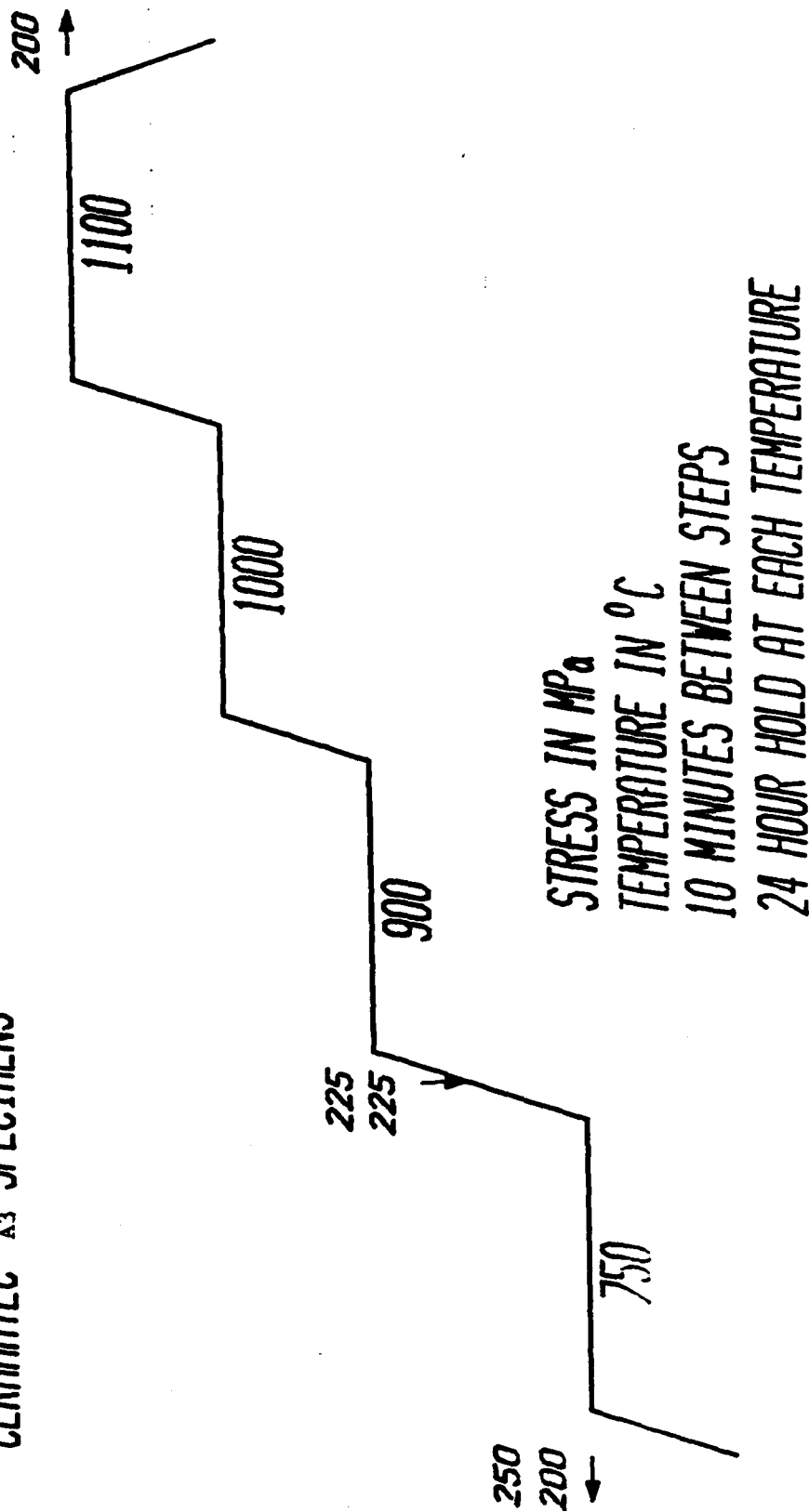
CERAMATEC A1 SPECIMENS

STRESS IN MPa
TEMPERATURE IN °C
10 MINUTES BETWEEN STEPS
24 HOUR HOLD AT EACH TEMPERATURE
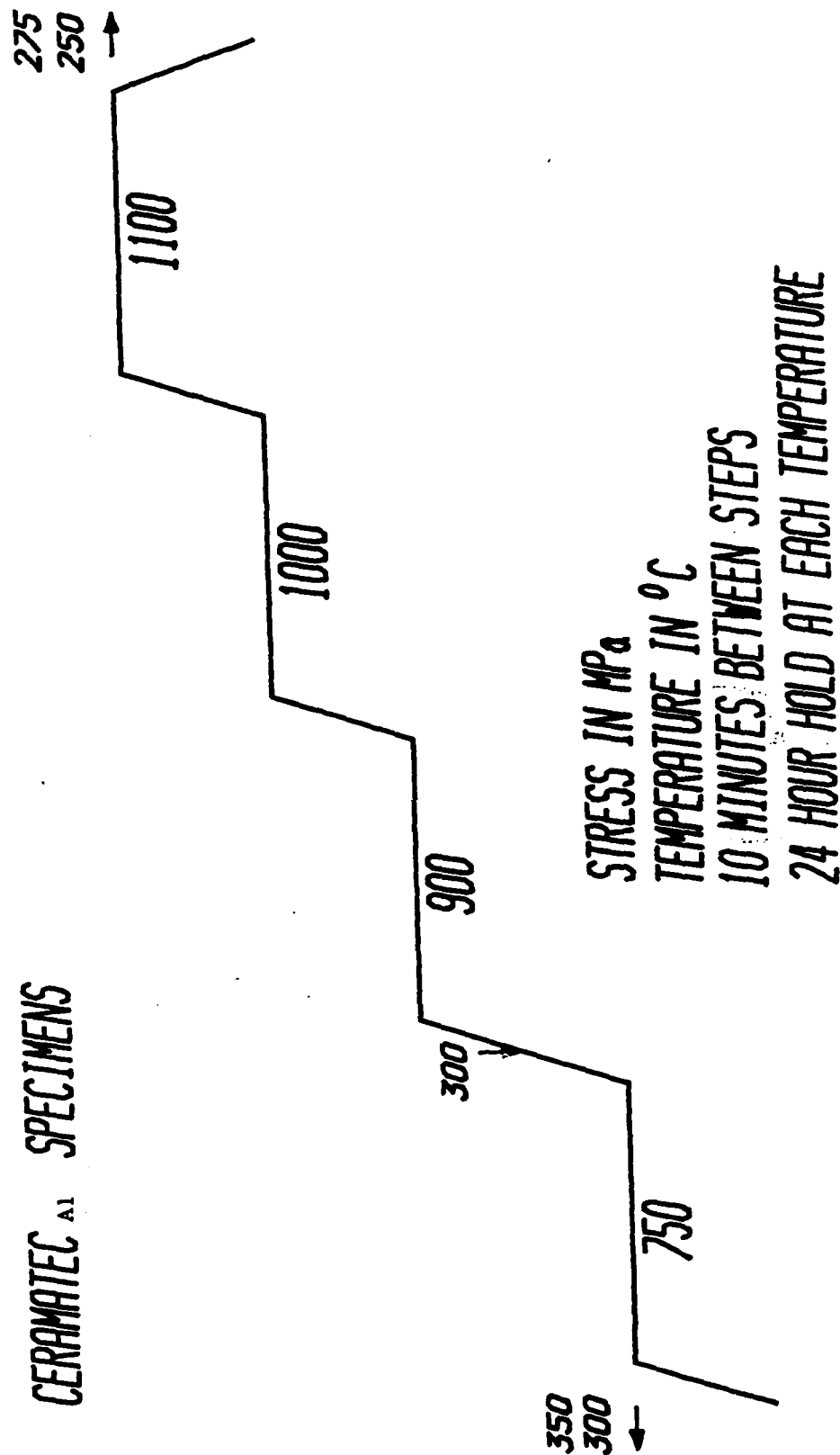
Figure#4: Stress rupture test of sample-A1.

STEPPED TEMPERATURE STRESS RUPTURE

CERAMATEC A2 SPECIMENS

STRESS IN MPa
TEMPERATURE IN °C
10 MINUTES BETWEEN STEPS
24 HOUR HOLD AT EACH TEMPERATURE
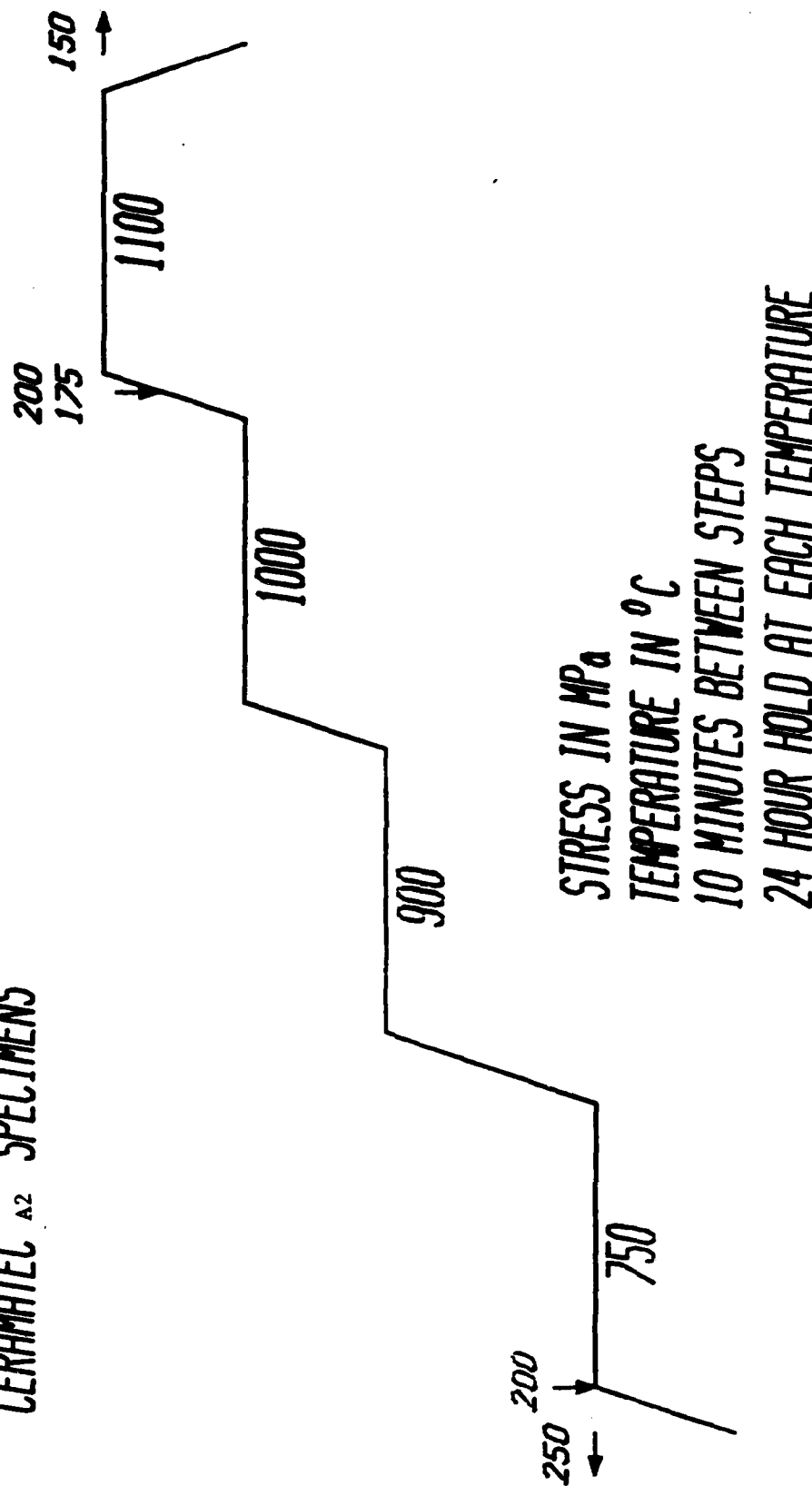
Figure#5: Stress rupture of sample-A2.

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STEPPED TEMPERATURE STRESS RUPTURE

CERAMATEC A3 SPECIMENS

STRESS IN MPa
TEMPERATURE IN °C
10 MINUTES BETWEEN STEPS
24 HOUR HOLD AT EACH TEMPERATURE

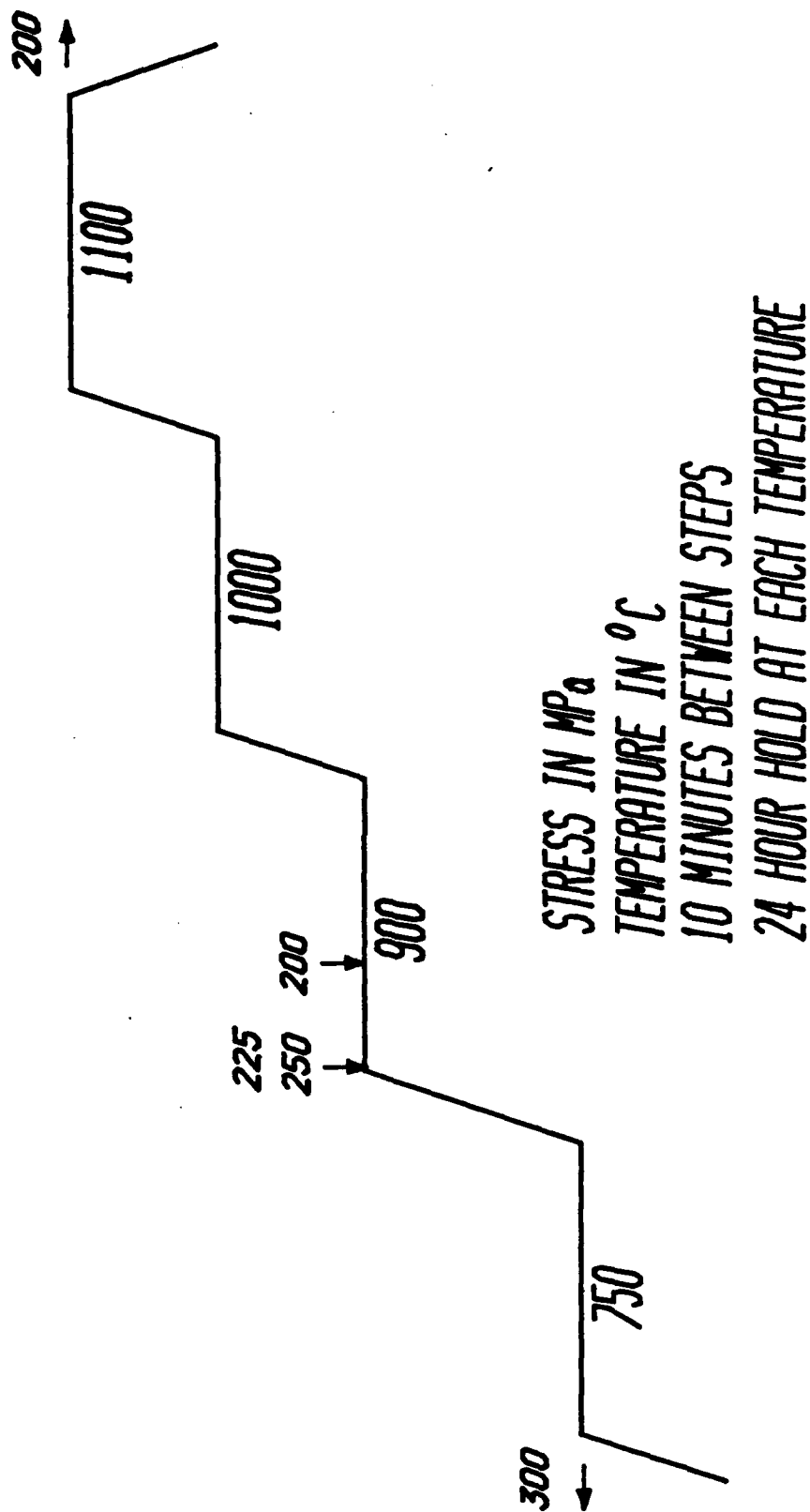Figure#6: Stress rupture test of sample-A3.

25
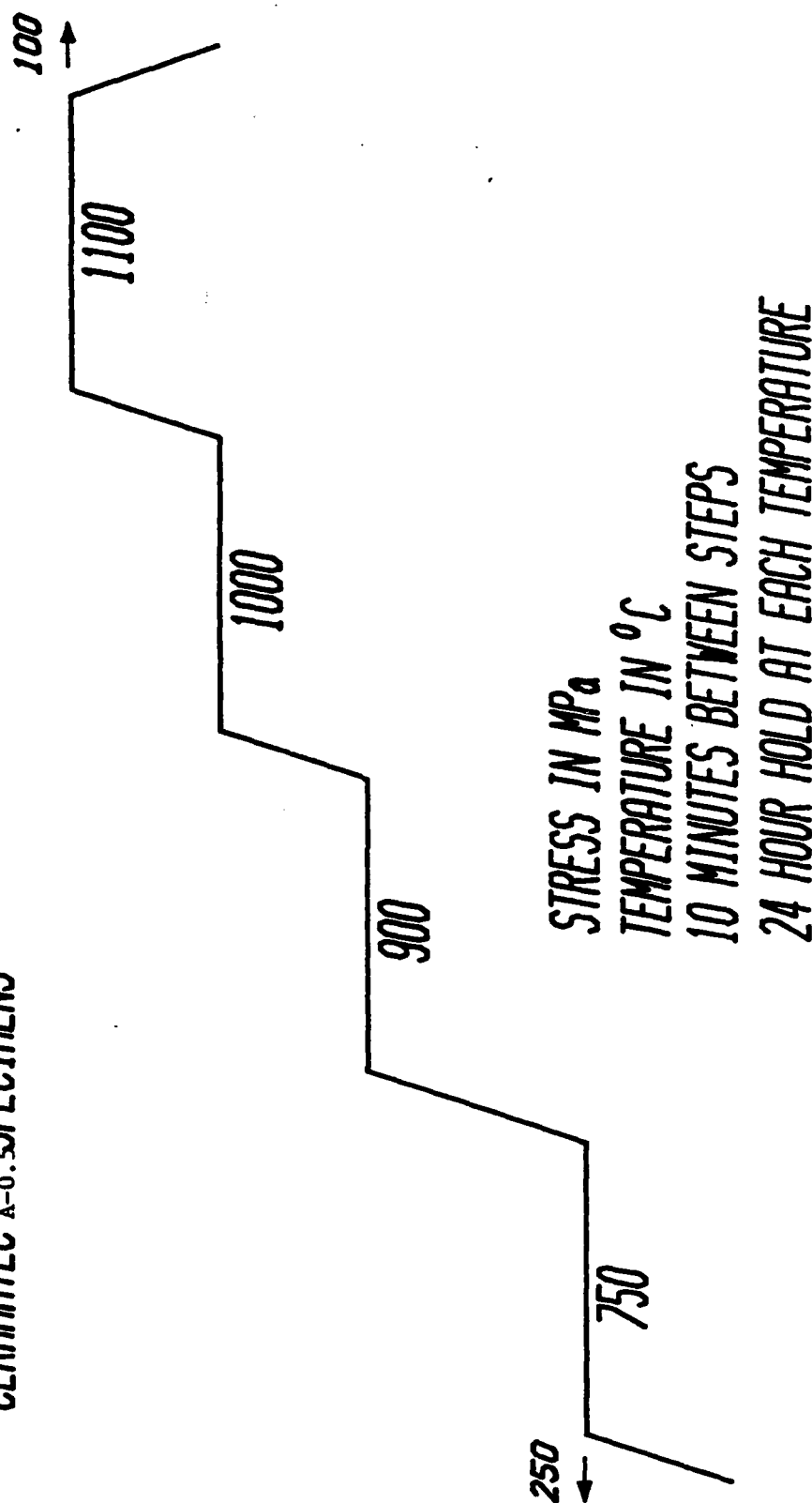
Figure#7: Stress rupture test of sample-A-0.5.
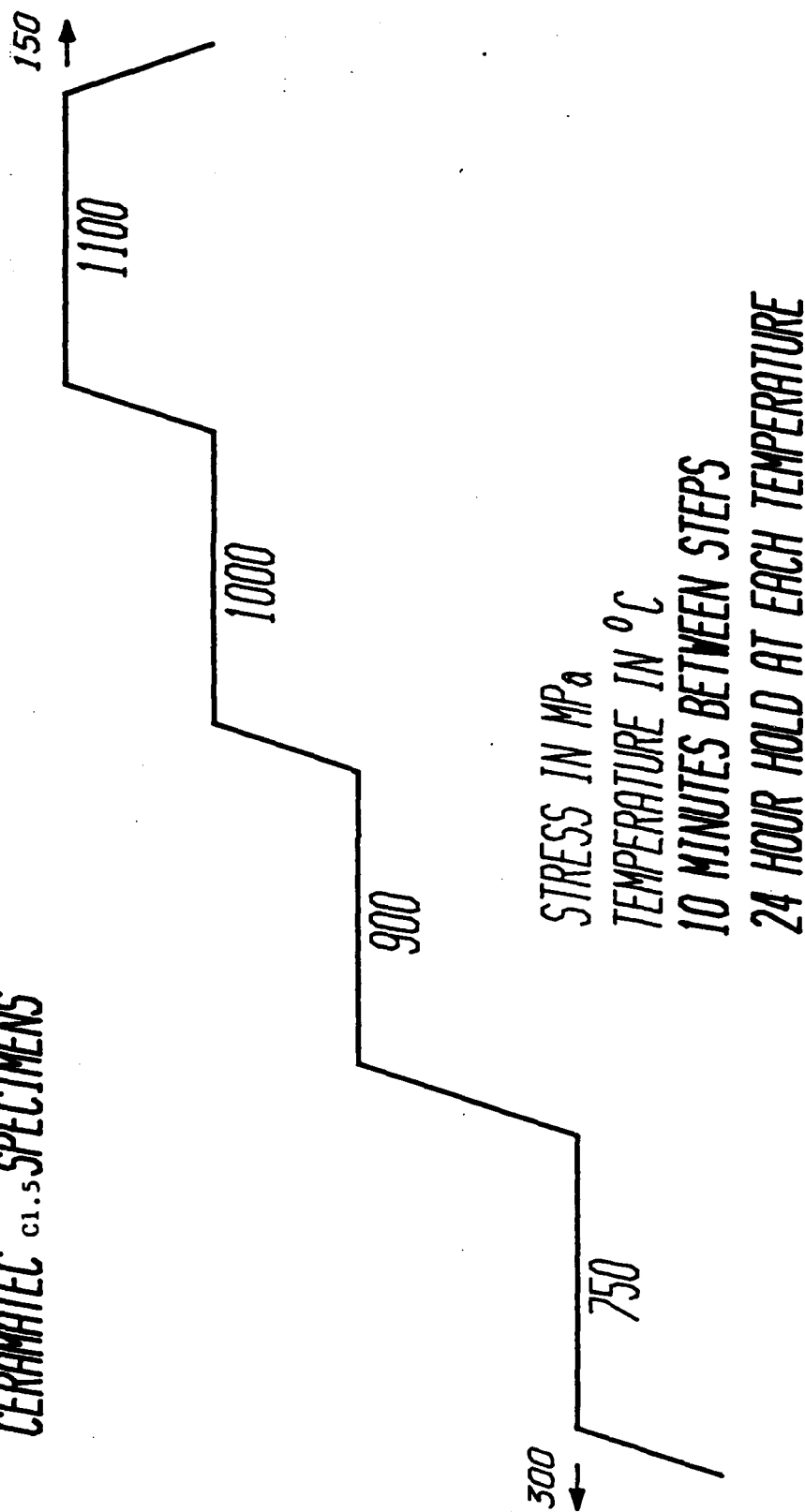
Figure#8: Stress rupture test of sample-C-0.5.

STEPPED TEMPERATURE STRESS RUPTURE

CERAMATEC C1.5 SPECIMENS

STRESS IN MPa
TEMPERATURE IN °C
10 MINUTES BETWEEN STEPS
24 HOUR HOLD AT EACH TEMPERATURE

Figure#9: Stress rupture test of sample-C-1.5.

X-Ray Diffraction Analysis

X-ray diffraction traces were obtained on as-fired and ground surfaces. X-ray diffraction traces were also obtained on fracture surfaces of some samples. The following specific observations were made.

(1) For the most part, as-sintered surfaces showed the existence of only the tetragonal polymorph of zirconia. The intensity of (002) peak is about half that of (200), as expected for random orientation of crystallites.

(2) After surface grinding, the intensity of (002) increased while that of (200) decreased. In many cases, the intensity of (002) became significantly greater than that of (200). This shows ferroelastic switching, as previously discussed[1,2].

(3) A small amount of monoclinic was formed on the ground surface. The amount of monoclinic phase was the least in samples doped with B. This appears to be consistent with the fact that, at room temperature, these samples have the lowest toughness.

(4) All peaks exhibited a significant amount of line broadening. Figures 10 and 11 show typical XRD patterns before and after surface grinding.

Fractography

All of the bend strength bars were examined under a low power, binocular optical microscope to locate the origin of fracture. Fracture origins were generally readily identifiable for samples broken at room temperature. Fracture origins were typically on the surface and pores appeared to be the fracture origins. This suggests that with improved processing, it should be possible to increase the strength. As mentioned previously,
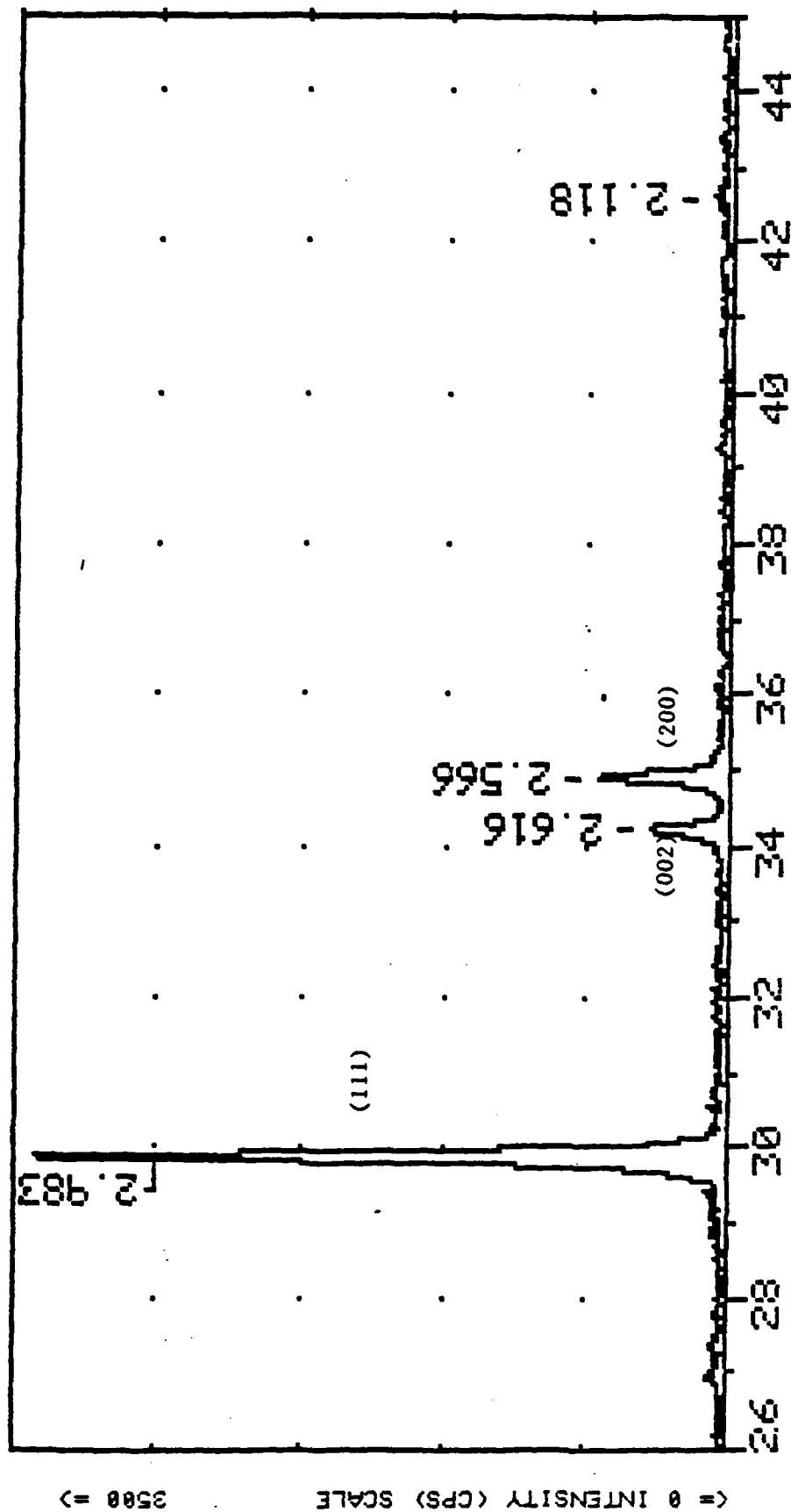
Figure#10: As-fired X-ray diffraction trace of sample-Al showing the presence of only the tetragonal polymorph. Also note that the intensity of the (002) peak is smaller than that of the (200) peak as expected of randomly oriented grain structure.
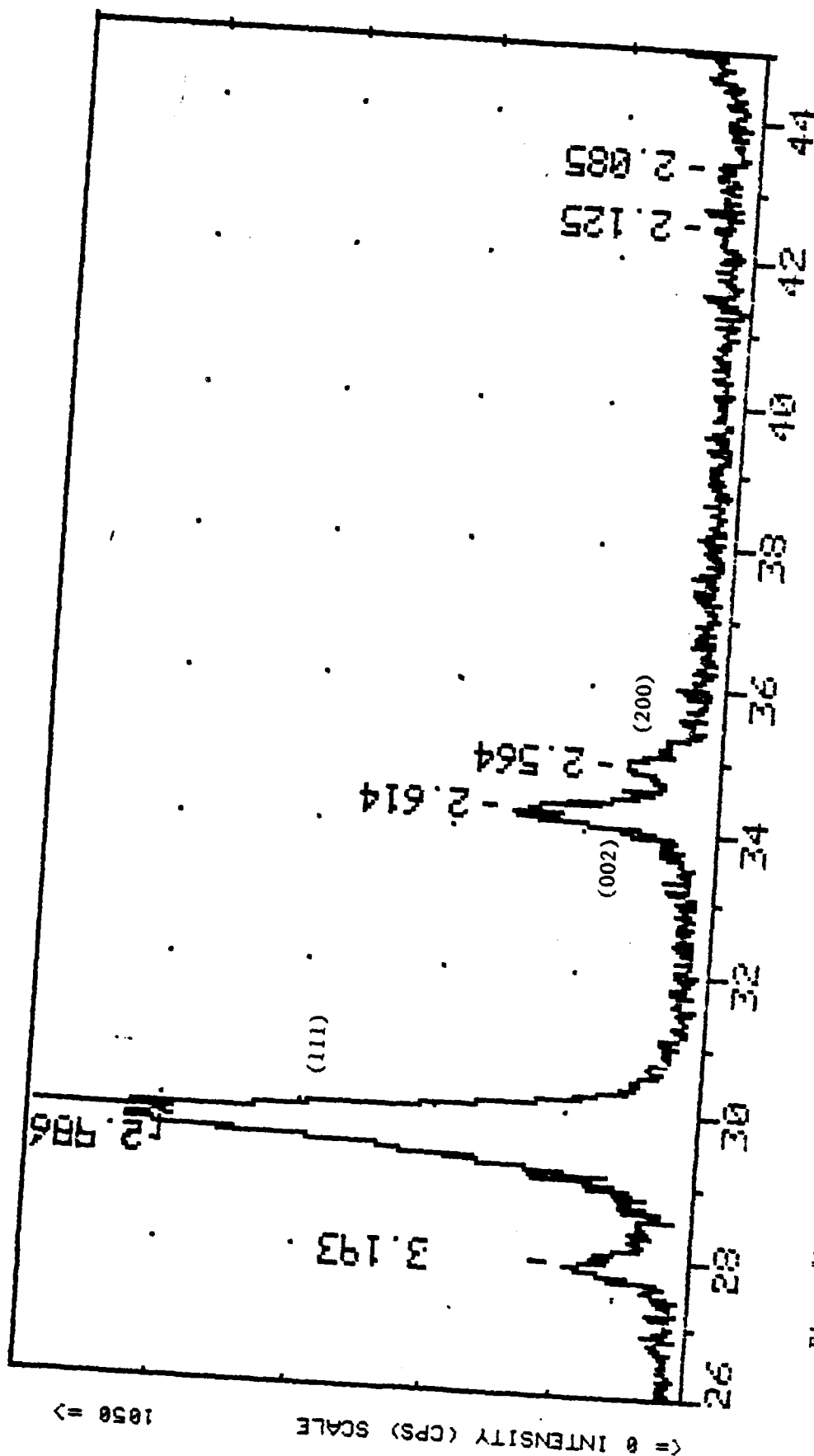
Figure#11: X-ray diffraction trace of sample-A1 after surface grinding. Note that a small amount of monoclinic phase has formed. The most significant change, however, is with respect to the (200) and the (002) peaks; specifically, the intensity of the (002) peak has increased while that of the (200) peak has decreased indicating ferroelastic domain switching.

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additions of dopants resulted in increased porosity. Recent work has shown that densities greater than 99% of theoretical can be achieved at all dopant levels by controlling sintering parameters.

Samples were also examined in a scanning electron microscope. It was observed that the dopants did not significantly affect the grain size of the material. The nature of the alumina phase, however, does seem to be affected by the addition of dopants. In the baseline material, alumina exists in equiaxed morphology. However, when dopant A is added, the resulting aluminate morphology is plate-like. This same behavior, to a varying degree, is exhibited by samples doped with B and C. This is apparently due to the reaction between the dopants and alumina to form aluminates. Figures 12 through 14 show typical SEM fractographs.

Figure 12.   Fracture surface of specimen A-3 (Ce-TZP with 3 wt.% A) showing tabular second phase (10,000X).

Figure 13.   F....... ...f...... .f .... (C...TZP with 3
wt.% ... . second .. .. 000X).

Figure 14.   Fracture surface of specimen C-3 (Ce-TZP with 3
wt.% C) showing tabular second phase (10,000X).

SUMMARY AND CONCLUSIONS

As part of Phase I effort, ceria-stabilized tetragonal polycrystalline zirconia (CeTZP) doped with three dopants, A, B and C, was characterized with regards to mechanical properties at temperatures up to 1100°C. Mechanical characterization included: (1) measurement of fracture toughness, K_{IC}, by both DCB and SENB techniques at room temperature, and by SENB technique at elevated temperatures, (2) measurement of flexural strength, and (3) stepped-temperature stress-rupture tests. Other characterization included determination of phases present by x-ray diffraction and microstructural characterization by scanning electron microscopy. Based on the work done, the following conclusions can be drawn:

(1) Dopants either enhance or suppress room temperature toughness; dopant A was found to enhance K_{IC}, while dopant B suppressed it. K_{IC} values as high as 14 $MPa.m^{1/2}$ were observed.

(2) Room temperature strength in excess of 600 MPa was observed. However, in most samples the strength decreased with increasing temperature indicating a substantial contribution of transformation toughening.

(3) In the second iteration, however, samples doped with A (A'-1) exhibited strength essentially independent of temperature. (Room temperature strength = 550 MPa, strength at 750°C = 470 MPa and strength at 1100°C = 400 MPa). This shows that it is possible to obtain high strengths at elevated temperatures. It is the objective of Phase II work to determine the fundamental mechanisms responsible for property retention at elevated temperatures, in particular the possible role of ferroelasticity. Microstructures of all doped samples exhibited the presence of tabular precipitates. The role of the precipitates or strength properties will be examined in Phase II.

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(4) Switching of x-ray peak intensities of (200)/(002) peaks upon grinding confirms that tetragonal zirconia used in the present study is ferroelastic. Phase II work will examine its possible role in toughening at strength retention at elevated temperatures.

ACKNOWLEDGEMENT

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REFERENCES

1. A.V. Virkar and R.L.K. Matsumoto, "Ferroelastic Domain Switching as a Toughening Mechanism in Tetragonal Zirconia," J. Am. Ceram. Co., 69 [10] C-224 - C-226 (1986).

2. A.V. Virkar and R.L.K. Matsumoto, "Toughening Mechanism in Tetragonal Zirconia Polycrystalline (TZP) Ceramics," to appear in Proceedings of the Third International Conference on The Science and Technology of Zirconia, Tokyo, Japan, 1986.

3. R.P. Ingel, D. lewis, B.A. Bender and R.W. Rice, "Temperature Dependence of Strength and Fracture Toughness of ZrO_2 Single Crystals," J. Am. Ceram. Soc., 65 [9] C-150-C-152 (1982).

4. J. Lankford, "Deformation of Transformation Toughened Zirconia," Advanced Structural Ceramics, Vol. 78, Ed. by P.F. Becher, M.V. Swain and S. Somiya, (MRS Soc. Pittsburgh, PA pp. 61-74 1987).

5. S.M. Wiederhorn, A.M. Shorb, and R.L. Moses, "Critical Analysis of the Theory of the Double Cantilever Method of Measuring Fracture-Surface Energies," J. Appl. Phys., 39 [3] 1569-72 (1968).

6. W.F. Brown and J.E. Srawley, "Plane Strain Crack Toughness Testing of High Strength Metallic Materials," ASTM Tech. Publ. 410, Philadelphia, PA, 1967.